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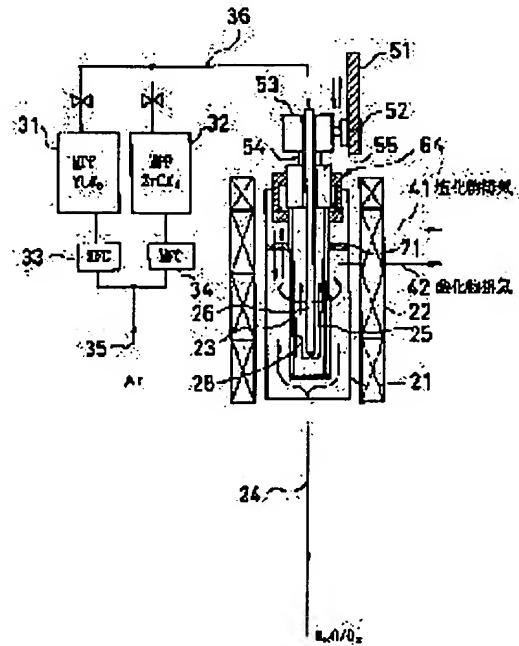
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(54) ELECTROCHEMICAL VAPOR DEPOSITION DEVICE AND FORMATION OF SOLID ELECTROLYTIC FILM

(57) Abstract:

PROBLEM TO BE SOLVED: To form a solid electrolytic film with a uniform film thickness on the inner circumference of an LSM tube.

SOLUTION: As for this electrochemical vapor deposition device, at the time of vaporizing vapor depositing raw material powder at, a high temp., introducing this into a reaction chamber 21 and electrochemically vapor-depositing a YSZ(yttria stabilized zirconia) solid electrolytic film 28 on the inner circumference of an LSM (porous strontium-added lanthanum manganite) tube 23, the LSM tube 23 is rotated around the axis and is moved in the axial direction, by which, even in the case that the flows of vapor depositing raw material vapor 25, an oxidizing gas 24 and the concn. thereof in the reaction



chamber 21 are ununiform, the vapor depositing raw material vapor 25 is vapor-deposited on each place of the inner circumference of the LSM tube 23 at a uniform film thickness to form a film of a YSZ solid electrolyte 28 with a uniform film thickness.

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CLAIMS**[Claim(s)]**

[Claim 1] Hold a tube-like vacuum evaporationo base in the interior, introduce the evaporated vacuum evaporationo raw material steam into the interior of said vacuum evaporationo base through steamy installation tubing, and oxidation gas is introduced into the exterior of said vacuum evaporationo base. Electrochemistry vacuum evaporationo equipment characterized by having a rotation means to rotate said vacuum evaporationo base to the circumference of a shaft, and a migration means to move said vacuum evaporationo base to shaft orientations, in the electrochemistry vacuum evaporationo equipment which equips the inner skin of said vacuum evaporationo base with the reaction chamber which forms the electrochemistry vacuum evaporationo film, and grows into it.

[Claim 2] Predetermined yttrium chloride powder and each zirconium chloride powder comparatively Draw by the predetermined flow rate, make it evaporate in an elevated-temperature ambient atmosphere, and a vacuum evaporationo raw material steam is generated. The membrane formation approach of the solid electrolyte using the electrochemistry vacuum evaporationo equipment according to claim 1 characterized by forming the electrochemistry vacuum evaporationo film in that inner skin while introducing this vacuum evaporationo raw material steam into said steamy installation tubing of said reaction chamber, and rotating said vacuum evaporationo base to the circumference of a shaft and making it move to shaft orientations.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the membrane formation approach of a solid electrolyte of having used electrochemistry vacuum evaporationo equipment and it.

[0002]

[Description of the Prior Art] Conventionally, there are a monotonous method and a cylinder method in a solid oxide fuel cell, and there are a pinstriped method and a disk method as cylinder method further. And especially the solid oxide fuel cell of a cylinder pinstriped method is structure shown in drawing 4. This conventional cylinder pinstriped method solid oxide fuel cell 106 is arranged in the form which makes it order from the inside at the laminated structure of the fuel electrode 103 made from the cermet of the air pole hanger tube 101 of porosity lanthanum comics night system oxide (LaMnO_x), the solid electrolyte 102 made from yttria stabilized zirconia (YSZ), nickel, cobalt, a nickel alloy or a cobalt alloy, and YSZ, and insulates an interconnector 104 from a fuel electrode 103 to a part of peripheral face, and is connected to the internal air pole hanger tube 101.

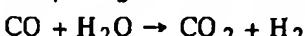
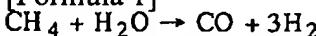
[0003] However, in the solid oxide fuel cell of such a conventional pinstriped cylinder method, there was a trouble which all the ingredients of each element are the products made from the ceramics, and stress concentrates on the neighborhood and the cell pars basilaris ossis occipitalis of an interconnector 104 which the dissimilar material from which especially coefficient of thermal expansion is different overlaps about 850-1050 degrees C in order to carry out operating at high temperatures, and a crack tends to generate.

[0004] Then, by JP,7-263001,A, the solid oxide fuel cell 110 of the structure shown in drawing 5 is proposed as what solves this conventional trouble. This solid oxide fuel cell 110 of the former proposed is characterized by the structure which inserts the conductive tube 111 for fuel supply in a core. That is, a fuel electrode 112, a solid electrolyte 113, and an air pole 114 are formed sequentially from the inside, the conductive tube 111 for fuel supply which made many holes in the core for fuel jet is inserted, and it is filled up with the conductive felt 115 which has a fuel reforming function between this conductive tube 111 and fuel electrode 112, and is the structure supply [structure] fuel gas 116 to the conductive tube 111, and it was made to circulate air 117 on a periphery.

[0005] When a generation-of-electrical-energy operation of this solid oxide fuel cell 110 is explained, supply fuel gas 116, such as natural gas, methane, and coal gasification gas, in the conductive tube 111 of a cell 110, the part of the conductive felt 115 is made to blow off through the tube wall of the porosity of the conductive tube 111, and the reforming reaction of the ** 1 following formula is made to usually cause under 650 degrees C - 1050 degrees C conditions under a high temperature condition in the part of this conductive felt 115, fuel electrode 112, and solid electrolyte 113.

[0006]

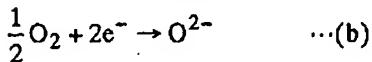
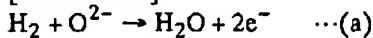
[Formula 1]



The generation-of-electrical-energy force is acquired by collecting a lifting and the electron which separated for the generation-of-electrical-energy reaction of the ** 2 following formula to the hydrogen generated at this reforming reaction in the part of the fuel electrode 112 and air pole 114 which carry out a counter electrode through a solid electrolyte 113.

[0007]

[Formula 2]



That is, as a fuel electrode 112 is shown in a ** 2 (a) type, the hydrogen generated at the reforming reaction reacts with the oxide ion supplied from a solid electrolyte 113, and generates a steam and an electron. And if the electron generated with the fuel electrode 112 arrives at an external circuit through an anode plate 119 the surroundings at an air pole 114 through the conductive felt 115 and the conductive tube 111 from cathode 118, it will set to this air pole 114. As shown in a ** 2 (b) type, it reacts with the oxygen in air 117, and oxide ion is generated, this is emitted to a solid electrolyte 113, reaches a fuel electrode 112 side, and the reaction of a ** 2 (a) type is presented with it.

[0008] In the fuel cell 110 of such a generator style, the parts of an air pole 114, a solid electrolyte 113, and a fuel electrode 112 are made like next, and are formed. As opposed to the base material of the porosity of a lanthanum comics night system which serves as an air pole 114 first Electrochemistry vacuum deposition, Thin using law that is, CVD(Chemical Vapor Deposition)-EVD (Electrochemical Vapor Deposition) -- The precise YSZ film is formed as a solid electrolyte 113. On this YSZ film further And nickel, The slurry coat of the powder of the alloy which uses cobalt, nickel, or cobalt as a principal component, or a nickel zirconia cermet is carried out. Membranes are formed using a spraying process which gives electrochemistry vacuum deposition similarly, and forms the porous fuel electrode 112, or is carried by JP,4-349343,A.

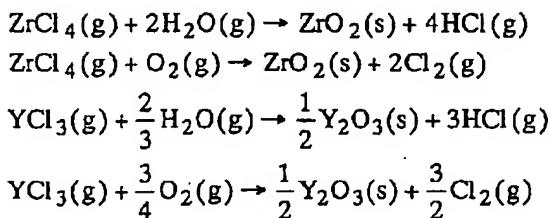
[0009] And as electrochemistry vacuum evaporationo equipment which forms a solid electrolyte 113, the thing of the structure shown in drawing 6 is used. This conventional electrochemistry vacuum evaporationo equipment sets the inside of a reaction chamber 21 to the condition near a vacuum, and about 1 Torr. At a heater 22 under about 1000-1200-degree C temperature conditions In the outside of the base 23 made from the strontium addition lanthanum comics night (LSM) of the porosity used as an air pole hanger tube, Argon Ar, The chloride YCl3 of the yttrium which introduces oxygen O2 and the mixed oxidization gas 24 of steam H2 O, and serves as a raw material of the YSZ film in other side faces, and a zirconium, and ZrCl4 A steam 25 is mixed in the argon (Ar) gas which is carrier gas, and it supplies from the raw material steamy supply pipe 26.

[0010] The supply network of this raw material steam 25 is a yttrium chloride YCl3 and a zirconium chloride ZrCl4. Raw material impalpable powder is stored in the powder feeders (MPF) 31 and 32. Even the raw material steamy supply pipe 26 of a reaction chamber 21 supplies through piping 36, mixing raw material impalpable powder in carrier gas 35 by supplying argon carrier gas 35 by the predetermined flow rate with massflow controllers (MFC) 33 and 34. It is the structure which evaporates with heating of a heater 22 within this raw material steamy supply pipe 26, makes the raw material steam 25, and is supplied in a reaction chamber 21.

[0011] By using the electrochemistry vacuum evaporationo equipment of such structure, as shown in drawing 7 (a), as the oxidation gas 24 which passes along many holes 27 of a base 23 at first, and the raw material steam 25 carry out the reaction shown in ** 3 formula and it is shown in drawing 7 (b), the YSZ film 28 is generated on the front face of a base 23, and many holes 27 of a base 23 are blockaded gradually. This is a CVD phase.

[0012]

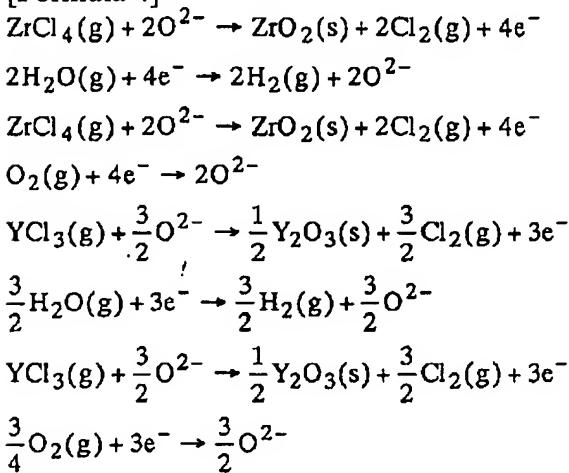
[Formula 3]



It is noted that the raw material steam 25 and oxidation gas 24 react directly after this CVD phase is completed, the oxygen from oxidation gas 24 is returned on a YSZ side, the inside of the YSZ film 28 is diffused as oxide ion O₂₋, and as it goes to a raw material chloride steam and the EVD phase of carrying out and the reaction shown in ** 4 formula is shown in this drawing (c), the YSZ film 28 grows.

[0013]

[Formula 4]



In this way, after carrying out slurry coating of the fuel electrode 112 further mentioned above after forming the YSZ film 28 as a solid electrolyte 113 with electrochemistry vacuum deposition, a fuel cell will be produced by the approach of carrying out electrochemistry vacuum evaporationo, and the other approaches.

[0014]

[Problem(s) to be Solved by the Invention] However, in the case of such conventional electrochemistry vacuum evaporationo equipment, there were the following troubles. As shown in drawing 6, the raw material steam 25 in a base 23 from lower limit opening of the raw material steamy supply pipe 26. Namely, discharge, Since the chloride exhaust air 41 which supplies oxidation gas to the outside of a base 23, and is generated at an EVD-CVD reaction, and oxide exhaust air 42 were structures discharged outside through the exhaust ports 43 and 44 prepared one place at a time in the upper part of a fission reactor 21, respectively, It was easy to produce the speed difference with the flow of gas in each part of the inside of a fission reactor 21, and there was a trouble which makes an ununiformity thickness of the solid electrolyte 28 which this vapor-deposits on the front face of a base 23.

[0015] This invention was made in view of such a conventional trouble, and it aims at offering the membrane formation approach of the solid electrolyte using the electrochemistry vacuum evaporationo equipment and it which can make thickness of a solid electrolyte uniform by making it move to shaft orientations while rotating a base during implementation of electrochemistry vacuum evaporationo.

[0016]

[Means for Solving the Problem] Invention of claim 1 holds a tube-like vacuum evaporationo base in the interior, introduces the evaporated vacuum evaporationo raw material steam into the interior of said vacuum evaporationo base through steamy installation tubing, and introduces oxidation gas into the exterior of said vacuum evaporationo base. In the electrochemistry vacuum evaporationo equipment which equips the inner skin of said vacuum evaporationo base with the reaction chamber which forms

the electrochemistry vacuum evaporationo film, and grows into it, it has a rotation means to rotate said vacuum evaporationo base to the circumference of a shaft, and a migration means to move said vacuum evaporationo base to shaft orientations.

[0017] By rotating a vacuum evaporationo base to the circumference of a shaft, and making it move to shaft orientations, in case vacuum evaporationo raw material powder is made to evaporate at an elevated temperature, it introduces into a reaction chamber with the electrochemistry vacuum evaporationo equipment of invention of claim 1 and the inner skin of a vacuum evaporationo base is made to carry out electrochemistry vacuum evaporationo Even if the flow of the vacuum evaporationo raw material steam in a reaction chamber and the flow of oxidation gas are uneven, surface every place of a vacuum evaporationo base are made to vapor-deposit a raw material steam by uniform thickness, and the uniform solid electrolyte of thickness is formed.

[0018] Invention of claim 2 is the membrane formation approach of the solid electrolyte using the electrochemistry vacuum evaporationo equipment indicated by claim 1. Predetermined yttrium chloride powder and each zirconium chloride powder comparatively The electrochemistry vacuum evaporationo film is formed in that inner skin, drawing by the predetermined flow rate, making it evaporate in an elevated-temperature ambient atmosphere, generating a vacuum evaporationo raw material steam, introducing this vacuum evaporationo raw material steam into said steamy installation tubing of said reaction chamber, and rotating said vacuum evaporationo base to the circumference of a shaft, and making it move to shaft orientations.

[0019] By the membrane formation approach of the solid electrolyte invention of claim 2, since a solid-electrolyte membrane is formed to the inner skin of a vacuum evaporationo base using the electrochemistry vacuum evaporationo equipment of claim 1, the solid-electrolyte membrane of uniform thickness can be formed over the whole inner skin of a vacuum evaporationo base.

[0020]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained in full detail based on drawing. Drawing 1 and drawing 2 show the electrochemistry vacuum evaporationo equipment of the gestalt of one operation of this invention. The electrochemistry vacuum evaporationo equipment of the gestalt of this 1st operation The inside of a reaction chamber 21 is set to the condition near a vacuum, and about 1 Torr like the conventional example shown in drawing 6. At a heater 22 under about 1000-1200-degree C temperature conditions In the outside of the LSM base 23 of the porosity used as an air pole hanger tube, Argon Ar, The yttrium which introduces oxygen O₂ and the mixed oxidation gas 24 of steam H₂O, and serves as a raw material of the YSZ film inside, The chloride YCl₃ of a zirconium, and ZrCl₄. It is the configuration which mixes a steam 25 in the argon (Ar) gas which is carrier gas, and is supplied from the raw material steamy supply pipe 26. Moreover, the supply network of the raw material steam 25 is a yttrium chloride YCl₃ and a zirconium chloride ZrCl₄. Raw material impalpable powder is stored in the powder feeders (MPF) 31 and 32. Even the raw material steamy supply pipe 26 of a reaction chamber 21 supplies through piping 36, mixing raw material impalpable powder in carrier gas 35 by supplying argon carrier gas 35 by the predetermined flow rate with massflow controllers (MFC) 33 and 34. It is the configuration which evaporates with heating of a heater 22 within this raw material steamy supply pipe 26, makes the raw material steam 25, and is supplied in a reaction chamber 21.

[0021] And the motor 53 is supported by the vertical perpendicular direction free [a slide] with the slider 52 which engaged with the slide base 51 fixed to the external holddown member (not shown), and it is fixed so that the rotation **** object 55 may rotate at a level with the surroundings of vertical axes to the rotation output shaft 54 of this motor 53. It binds tight to the inferior-surface-of-tongue side of the rotation **** object 55, and the upper limit section of the LSM base 23 is being fixed with the ring 56. In addition, bleeder 23a for discharging the chloride exhaust air mentioned later shall be formed in the upper part (part which does not form a solid-electrolyte membrane) of the LSM base 23 at two or more places.

[0022] On the other hand, the female screw section 61 is formed in the upper part, and the support barrel 64 in which the slide guide 63 in which O ring 62 after which it runs to the lower part was inserted was

formed is being fixed to the upper limit section of a reaction chamber 21. Moreover, the bleeder 65 for chloride exhaust air is formed in two or more locations at the support barrel 64. And the above-mentioned rotation **** object 55 is made to screw in the female screw section 61 of this support barrel 64.

[0023] In the downward location, the dashboard 71 is attached in the interior of a reaction chamber 21 in airtight rather than the support barrel 64. O ring 72 is inserted in the inner circumference section of this dashboard 71, and it is contacted to the peripheral face of the LSM base 23 in airtight and possible [a slide]. And in the location of this dashboard 71 top, the exhaust port 73 for chloride exhaust air is formed in a reaction chamber 21, and the exhaust port 74 for oxide exhaust air is formed in the reaction chamber 21 in the location of the dashboard 71 bottom.

[0024] In addition, sealing of the raw material steamy supply pipe 26 is carried out in airtight, and these motors 53, the rotation output shaft 54, the rotation **** object 55, and the bolting ring 56 rotate in airtight to the raw material steamy supply pipe 26, and it enables it to be piped so that each core of a motor 53, the rotation output shaft 54, the rotation **** object 55, and the bolting ring 56 may be penetrated, and to have slid it with the sealing means (not shown).

[0025] Next, the procedure of the solid electrolyte membrane formation by the electrochemistry vacuum evaporationo equipment of the above-mentioned configuration is explained. A yttrium chloride YCl₃ and chlorination zirconia ZrCl₄ Raw material impalpable powder is stored in the powder feeders (MPF) 31 and 32. The raw material which raw material impalpable powder mixed in carrier gas 35 by supplying argon carrier gas 35 by the predetermined flow rate with massflow controllers (MFC) 33 and 34 (-- for example, ZrCl₄ : Supply mixed) to the raw material steamy supply pipe 26 at the rate of 4 - 10 g/hr extent through piping 36 at the weight ratio of YCl₃ = 5:1, with heating of a heater 22, make a raw material evaporate, make it a raw material steam, and supply from the lower part inside the LSM base 23 in a reaction chamber 21.

[0026] The inside of a reaction chamber 21 is set to the condition near a vacuum, and about 1 Torr, and is about 1000-1200-degree C temperature conditions by the heater 22. In the outside of the LSM base 23 of the porosity used as an air pole hanger tube, Argon Ar, They are 0.4-2.0l. / min about oxygen O₂ and the mixed oxidation gas 24 of steam H₂O. It introduces by the flow rate. The chloride YCl₃ of the yttrium which serves as a raw material of the YSZ film inside, and a zirconium, and ZCl₄ A steam 25 is mixed in the argon Ar which is carrier gas, and it supplies from the lower limit section of the raw material steamy supply pipe 26. The YSZ film 28 is formed as a solid-electrolyte membrane by the CVD-EVD operation shown in drawing 7 by this at the medial surface of a base 23.

[0027] And by carrying out forward inverse rotation of the motor 53 during supply of this raw material steam 25, and carrying out forward inverse rotation of the rotation **** object 55 slowly through the rotation output shaft 54, vertical migration is carried out with a motor 53, rotating the rotation **** object 55 by screwing with the female screw section 1 of the support barrel 64 of the upper part of a reaction chamber 21, and vertical migration is carried out, also rotating the base 23 attached in this. The rotational speed of a base 23 is crawling [of 0.005 - 0.05rpm]. Even if there is offset of dispersion, such as temperature conditions in the rate of the raw material steam 25, concentration, and a reaction chamber 21, or a medial axis, the YSZ film 28 is vapor-deposited by thickness uniform to each part of the medial surface of a base 23 by this.

[0028] in addition, CVD-EVD -- the chloride exhaust air 41 born by law is discharged outside by the room of the dashboard 71 top in a reaction chamber 21 through an exhaust port 73 through the bleeder 65 of bleeder 23a of the base 23 upper part, and the support barrel 64 from an assembly and here. Moreover, oxide exhaust air 42 is discharged outside through an exhaust port 74 by the dashboard 72 bottom in a reaction chamber 21 from an assembly and here.

[0029] thus, by the solid electrolyte membrane formation approach using the electrochemistry vacuum evaporationo equipment of the gestalt of this 1st operation Since it is made to move up and down in case the solid electrolyte YSZ film 28 is formed by the CVD-EVD method at a base 23, rotating a base 23 in a reaction chamber 21 It is the upper and lower sides in a reaction chamber 21, and even if there is dispersion, such as a rate of the raw material steam 25, concentration, and temperature conditions, by the

circumferencial direction, the YSZ film 28 can vapor-deposit by uniform thickness to each part of the medial surface of a base 23.

[0030] Next, the electrochemistry vacuum evaporationo equipment of the gestalt of operation of the 2nd of this invention is explained based on drawing 3. The electrochemistry vacuum evaporationo equipment of the gestalt of the 2nd operation is the yttrium chloride YCl₃ which it has the raw material liquid reservoir sections 81 and 82, and is raw material impalpable powder. Zirconium chloride ZrCl₄ Each is diluted by the ethanol as a diluent, and it is made mixed liquor, and stores here temporarily. the raw material liquid stored by these raw material liquid reservoir sections 81 and 82 -- massflow controllers (MFC) 83 and 84 -- it controls to discharge a constant rate to fixed time amount as be alike, respectively.

[0031] The structure of a reaction chamber 21 and the structure of the rotation and the sliding mechanism to the base 23 in a reaction chamber 21 are the same as the gestalt of the 1st operation shown in drawing 1 and drawing 2.

[0032] Next, the procedure of solid electrolyte membrane formation using the electrochemistry vacuum evaporationo equipment of the gestalt of this 2nd operation is explained. each impalpable powder of a yttrium chloride and a zirconium chloride -- a suitable quantity of ethanol -- mixing -- raw material mixed liquor -- creating -- these -- the raw material liquid reservoir sections 81 and 82 -- it is alike, respectively and is made to store

[0033] A reaction chamber 21 is decompressed to the atmospheric pressure near a vacuum, and about 1 Torr extent, and is further heated to the temperature of 1000-1200 degrees C at a heater 22. And they are 0.4-2.0l. / min about the mixed oxidation gas 24 of an argon, a steam, and oxygen. The outside of the base 23 in a reaction chamber 21 is supplied by the flow rate.

[0034] As opposed to the raw material liquid currently stored by the raw material reservoir sections 81 and 82 after such a reserve process Argon gas is supplied by the predetermined flow rate with massflow controllers 83 and 84. These raw material liquid For example, the amount of supply of both raw material liquid converts into the weight of the raw material powder contained in it, and supplies by the flow rate of 4 - 10 g/hr extent in total. The yttrium chloride which heated at the evaporation room which is not illustrated, was made to carry out evaporation decomposition of the diluent, and remained further, After making a zirconium chloride evaporate, the raw material steamy supply pipe 26 is supplied with the argon gas Ar which is carrier gas, and this raw material steamy supply pipe 26 to the raw material steam 25 is supplied from the lower part inside the LSM base 23 in a reaction chamber 21.

[0035] And vertical migration is carried out by rotating a motor 53 during supply of this raw material steam 25, and rotating the rotation **** object 55 slowly through the rotation output shaft 54, rotating a base 23 with the rotation **** object 55.

[0036] The YSZ film 28 can be formed for this procedure as a solid-electrolyte membrane to the medial surface of a base 23 according to a CVD-EVD operation like the gestalt of the 1st operation predetermined time, for example, by continuing for 5 hours. And since vertical migration is carried out while a base 23 rotates, each part of the medial surface of a base 23 can be made to vapor-deposit the YSZ film 28 by uniform thickness, even if there is dispersion, such as temperature conditions in the rate of the raw material steam 25, concentration, and a reaction chamber 21.

[0037]

[Example] The YSZ solid electrolyte was formed using the electrochemistry vacuum evaporationo equipment shown in <example 1> drawing 1 and drawing 2. Therefore, LSM tubing (outer-diameter 21mmphi, bore 17mmphi, die length of 50cm) of the base 23 which forms an air pole hanger tube was attached in the lower part of the rotation **** object 55 in the reaction chamber 21, and outer-diameter 12mmphi and the raw material steamy supply pipe 26 made from carbon with a bore [phi] of 9mm were attached in the core of a reaction chamber 21. And a reaction chamber 21 is made into a vacuum to 1Torr extent, it heats at 1200 degrees C at a heater 22, and they are 0.5l. / min about the oxidation gas 24 of an argon / steam / oxygen to the outside of the base 23 of a reaction chamber 21 further. It supplied by the flow rate.

[0038] A yttrium chloride and the impalpable powder of each zirconium chloride with massflow

controllers 33 and 34 and by the weight ratio of 1:5 And supply an evaporation room (not shown) by the flow rate which converts into raw material powder weight and serves as 5g / hr extent in great numbers, heat at 1200 degrees C, make them evaporate, and it considers as a raw material steam. This was further supplied inside the base 23 of a reaction chamber 21 from the raw material steamy supply pipe 26, electrochemistry vacuum evaporationo of 5 hours was performed, and about 50-micrometer YSZ solid-electrolyte membrane 28 was formed. Vertical migration was carried out from the lowest location to the best location during this electrochemistry vacuum evaporationo by carrying out forward inverse rotation of the raw material steamy supply pipe 26 to ***** by 0.01rpm by the motor 53.

[0039] The obtained solid-electrolyte membrane was precise and uniform thickness.

[0040] A yttrium chloride and the raw material liquid which mixed the impalpable powder of each zirconium chloride with ethanol to 1:1 by the weight ratio using the electrochemistry vacuum evaporationo equipment shown in <example 2> drawing 3 at a rate of 1:5 Equipment is supplied by the flow rate which converts into raw material powder weight and serves as 5 g/hr extent in great numbers, it heats at 1200 degrees C and evaporation decomposition of the diluent is carried out, and raw material powder is made to evaporate and it is made a raw material steam. This as well as an example 1 and in the vacuum of 1Torr extent Electrochemistry vacuum evaporationo was performed supplying through the raw material steamy supply pipe 26 inside the base 23 of a reaction chamber 21 heated at 1200 degrees C. A setup of the rotational speed of a base 23 was made the same as an example 1.

[0041] The obtained YSZ solid-electrolyte membrane 28 was about 50 micrometers, and was precise and uniform thickness.

[0042]

[Effect of the Invention] By rotating a vacuum evaporationo base to the circumference of a shaft, and making it move to shaft orientations, in case according to the electrochemistry vacuum evaporationo equipment of invention of claim 1 vacuum evaporationo raw material powder is made to evaporate, it introduces into a reaction chamber and the inner skin of a vacuum evaporationo base is made to carry out electrochemistry vacuum evaporationo as mentioned above Even if the flow of the vacuum evaporationo raw material steam in a reaction chamber and the flow of oxidation gas are uneven, surface every place of a vacuum evaporationo base can be made to be able to vapor-deposit a vacuum evaporationo raw material steam by uniform thickness, and the uniform solid electrolyte of thickness can be formed.

[0043] According to the membrane formation approach of the solid electrolyte invention of claim 2, since a solid-electrolyte membrane is formed to the inner skin of a vacuum evaporationo base using the electrochemistry vacuum evaporationo equipment of invention of claim 1, the solid-electrolyte membrane of uniform thickness can be formed over the whole inner skin of a vacuum evaporationo base.

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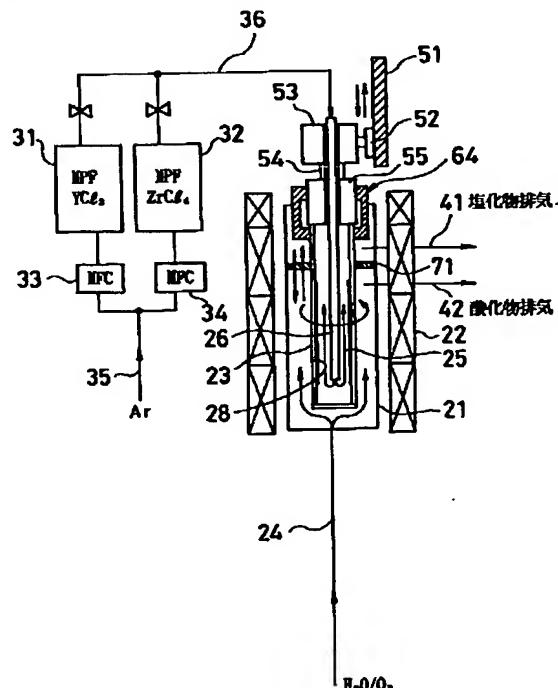
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(54)【発明の名称】 電気化学蒸着装置及びそれを用いた固体電解質の成膜方法

(57)【要約】

【課題】 LSM管の内周に均一な膜厚の固体電解質膜を成膜する。

【解決手段】 この発明の電気化学蒸着装置は、蒸着原料粉末を高温で気化させ、反応室21に導入してLSM管23の内周面にYSZ固体電解質膜28を電気化学蒸着させる際に、LSM管23を軸周りに回転させ、かつ軸方向に移動させることによって、反応室21内の蒸着原料蒸気25や酸化ガス24の流れ、濃度が不均一であってもLSM管23の内周面各所に均一な膜厚で蒸着原料蒸気を蒸着させ、膜厚の均一なYSZ固体電解質28を成膜する。



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【特許請求の範囲】

【請求項1】 円管状の蒸着基体を内部に収容し、かつ酸化された蒸着原料蒸気を蒸気導入管を通じて前記蒸着基体の内部に導入し、かつ前記蒸着基体の外部に酸化ガスを導入して、前記蒸着基体の内周面に電気化学蒸着膜を形成する反応室を備えて成る電気化学蒸着装置において、

前記蒸着基体を軸周りに回転させる回転手段と、前記蒸着基体を軸方向に移動させる移動手段とを備えたことを特徴とする電気化学蒸着装置。

【請求項2】 塩化イットリウム粉末、塩化ジルコニア粉末それぞれを所定の割合、所定の流量で導出し、高温雰囲気で酸化させて蒸着原料蒸気を生成し、この蒸着原料蒸気を前記反応室の前記蒸気導入管に導入して前記蒸着基体を軸周りに回転させ、かつ軸方向に移動させながらその内周面に電気化学蒸着膜を形成することを特徴とする請求項1に記載の電気化学蒸着装置を用いた固体電解質の成膜方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、電気化学蒸着装置及びそれを用いた固体電解質の成膜方法に関する。

【0002】

【従来の技術】 従来、固体電解質型燃料電池には平板方式と円筒方式とがあり、さらに円筒方式には縦縞方式と横縞方式がある。そして特に、円筒縦縞方式の固体電解質型燃料電池は図4に示す構造である。この従来の円筒縦縞方式固体電解質型燃料電池106は、内側から順に多孔質ランタンマンガナイト系酸化物(LaMnO_x)の空気極支持管101、イットリア安定化ジルコニア(YSZ)製の固体電解質102、ニッケル、コバルト、ニッケル合金又はコバルト合金とYSZとのサーメット製の燃料極103の積層構造にして、外周面の一部にインタコネクタ104を燃料極103から絶縁し、かつ内部の空気極支持管101に接続する形で配置している。

【0003】 しかしながら、このような従来の縦縞円筒方式の固体電解質型燃料電池では、各要素の材料がすべてセラミックス製で、かつ約850～1050℃の高温で作動するため、特に熱膨張率の違う異種材料が重なり合うインタコネクタ104の付近や電池底部に応力が集中してクラックが発生しやすい問題点があった。

【0004】 そこで、この従来の問題点を解決するものとして、特開平7-263001号公報では、図5に示す構造の固体電解質型燃料電池110が提案されている。この提案されている従来の固体電解質型燃料電池110は、中心部に燃料供給用導電性チューブ111を挿入する構造を特徴としている。すなわち、内側から順に燃料極112、固体電解質113、空気極114を形成し、中心部に燃料噴出のために多数の穴を開けた燃料供

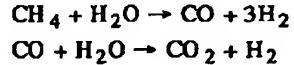
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給用導電性チューブ111を挿入し、この導電性チューブ111と燃料極112との間に燃料改質機能を持つ導電性フェルト115を充填し、そして導電性チューブ111に燃料ガス116を供給し、外周に空気117を流通させるようにした構造である。

【0005】 この固体電解質型燃料電池110の発電作用について説明すると、電池110の導電性チューブ111内に天然ガス、メタン、石炭ガス化ガスなどの燃料ガス116を供給し、導電性チューブ111の多孔質の管壁を通して導電性フェルト115の部分に噴出させ、この導電性フェルト115と燃料極112と固体電解質113の部分で高温度条件下、通常、650℃～1050℃の条件下で次の化1式の改質反応を起こさせる。

【0006】

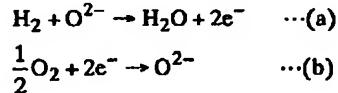
【化1】



この改質反応で発生する水素に対して、固体電解質113を介して対極する燃料極112と空気極114との部分で次の化2式の発電反応を起こし、遊離した電子を集めることによって発電力を得る。

【0007】

【化2】



つまり、燃料極112においては化2(a)式に示すように、改質反応で生成された水素が、固体電解質113から供給される酸化物イオンと反応して水蒸気と電子を生成する。そして燃料極112で生成された電子が導電性フェルト115と導電性チューブ111を経て陰極118から外部回路に回り、陽極119を経て空気極114に到達すると、この空気極114において、化2(b)式に示すように空気117中の酸素と反応して酸化物イオンを生成し、これが固体電解質113に放出され、燃料極112側に到達して化2(a)式の反応に供されるのである。

【0008】 このような発電機構の燃料電池110において、空気極114、固体電解質113及び燃料極112の部分は次のようにして形成している。まず空気極114となるランタンマンガナイト系の多孔質の基材に対して電気化学蒸着法、つまり、CVD(Chemical Vapor Deposition)-EVD(Electrochemical Vapor Deposition)法を用いて薄く、かつ緻密なYSZ膜を固体電解質113として形成し、さらにこのYSZ膜にニッケル、コバルト、ニッケル又はコバルトを主成分とする合金、あるいはニッケルジルコニアサーメットの粉末を50スラリーコートし、同じように電気化学蒸着法を施して

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多孔質の燃料極112を成膜し、あるいは特開平4-3
49343号公報に掲載されているような溶射法を用いて成膜するのである。

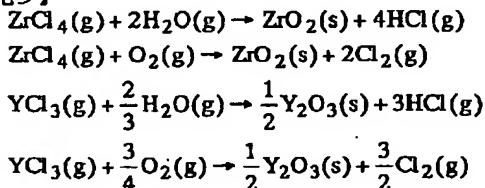
【0009】そして固体電解質113の成膜を行う電気化学蒸着装置としては、図6に示す構造のものが使用されている。この従来の電気化学蒸着装置は、反応室21内を真空に近い状態、約1 Torrにして、かつヒータ22によって約1000~1200°Cの温度条件下で、空気極支持管となる多孔質のストロンチウム添加ランタンマンガナイト(LSM)製の基体23の外側にはアルゴンAr、酸素O₂、水蒸気H₂Oの混合酸化ガス24を導入し、他側面にはYSZ膜の原料となるイットリウム、ジルコニウムの塩化物YC₁₃、ZrC₁₄の蒸気25をキャリアガスであるアルゴン(Ar)ガスに混入して原料蒸気供給管26から供給する。

【0010】この原料蒸気25の供給系統は、塩化イットリウムYC₁₃、塩化ジルコニウムZrC₁₄の原料微粉末をパウダーフィーダ(MPF)31、32に貯留しておき、マスフローコントローラ(MFC)33、34によって所定の流量でアルゴンキャリアガス35を供給することによってキャリアガス35に原料微粉末を混入しつつ配管36を通じて反応室21の原料蒸気供給管26まで供給し、この原料蒸気供給管26内でヒーター22の加熱によって気化し、原料蒸気25にして反応室21内に供給する構造である。

【0011】このような構造の電気化学蒸着装置を使用することによって、図7(a)に示すように、最初は基体23の多数の孔27を通ってくる酸化ガス24と原料蒸気25とが化3式に示す反応をして図7(b)に示すようにYSZ膜28を基体23の表面に生成し、徐々に基体23の多数の孔27を閉塞していく。これがCVD段階である。

【0012】

【化3】

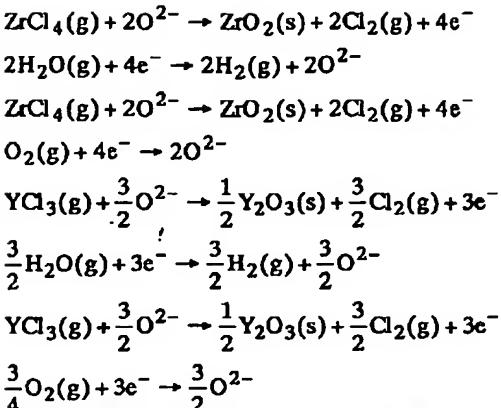


このCVD段階が終了すると、原料蒸気25と酸化ガス24とは直接に反応することはなくなり、酸化ガス24からの酸素がYSZ面上で還元されてYSZ膜28中を酸化物イオンO²⁻として拡散し、化4式に示す反応を原料塩化物蒸気と行うEVD段階へ進み、同図(c)に示すようにYSZ膜28が成長する。

【0013】

【化4】

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こうして電気化学蒸着法によって固体電解質113としてYSZ膜28を成膜した後は、さらに上述した燃料極112をスラリーコーティングした後に電気化学蒸着する方法、その他の方法で燃料電池を作製することになる。

【0014】

【発明が解決しようとする課題】しかしながら、このような従来の電気化学蒸着装置の場合、次のような問題点があった。すなわち、図6に示すように原料蒸気供給管26の下端開口部から原料蒸気25を基体23内に吐出し、基体23の外側に酸化ガスを供給し、EVD-CVD反応で発生する塩化物排気41、酸化物排気42はそれぞれ、反応炉21の上部に一個所ずつ設けられた排出口43、44を通じて外部に排出する構造であったため、反応炉21内各部でガスの流れに速度差が生じやすく、これが基体23の表面に蒸着する固体電解質28の膜厚を不均一にする問題点があった。

【0015】本発明はこのような従来の問題点に鑑みてなされたもので、電気化学蒸着の実施中に基体を回転させると共に軸方向に移動させることによって固体電解質の膜厚を一様にすることができる電気化学蒸着装置及びそれを用いた固体電解質の成膜方法を提供すること目的とする。

【0016】

【課題を解決するための手段】請求項1の発明は、円管状の蒸着基体を内部に収容し、かつ気化された蒸着原料蒸気を蒸気導入管を通じて前記蒸着基体の内部に導入

し、かつ前記蒸着基体の外部に酸化ガスを導入して、前記蒸着基体の内周面に電気化学蒸着膜を形成する反応室を備えて成る電気化学蒸着装置において、前記蒸着基体を軸周りに回転させる回転手段と、前記蒸着基体を軸方向に移動させる移動手段とを備えたものである。

【0017】請求項1の発明の電気化学蒸着装置では、蒸着原料粉末を高溫で気化させ、反応室に導入して蒸着基体の内周面に電気化学蒸着させる際に、蒸着基体を軸周りに回転させ、かつ軸方向に移動させることによつて、反応室の蒸着原料蒸気の流れや酸化ガスの流れが

50 不均一であっても蒸着基体の表面各所に均一な膜厚で原

料蒸気を蒸着させ、膜厚の均一な固体電解質を成膜する。

【0018】請求項2の発明は、請求項1に記載された電気化学蒸着装置を用いた固体電解質の成膜方法であって、塩化イットリウム粉末、塩化ジルコニウム粉末それを所定の割合、所定の流量で導出し、高温雰囲気で気化させて蒸着原料蒸気を生成し、この蒸着原料蒸気を前記反応室の前記蒸気導入管に導入して前記蒸着基体を軸周りに回転させ、かつ軸方向に移動させながらその内周面に電気化学蒸着膜を形成するものである。

【0019】請求項2の発明の固体電解質の成膜方法では、請求項1の電気化学蒸着装置を用いて蒸着基体の内周面に固体電解質膜を成膜するので、蒸着基体の内周面全体に渡り、均一な膜厚の固体電解質膜を成膜することができる。

【0020】

【発明の実施の形態】以下、本発明の実施の形態を図に基づいて詳説する。図1及び図2は、本発明の1つの実施の形態の電気化学蒸着装置を示している。この第1の実施の形態の電気化学蒸着装置は、図6に示した従来例と同様に反応室21内を真空中に近い状態、約1 Torrにして、かつヒータ22によって約1000～1200°Cの温度条件下で、空気極支持管となる多孔質のLSM基体23の外側にはアルゴンAr、酸素O₂、水蒸気H₂Oの混合酸化ガス24を導入し、内側にはYSZ膜の原料となるイットリウム、ジルコニウムの塩化物YC1₃、ZrC1₄の蒸気25をキャリアガスであるアルゴン(Ar)ガスに混入して原料蒸気供給管26から供給する構成である。また原料蒸気25の供給系統は、塩化イットリウムYC1₃、塩化ジルコニウムZrC1₄の原料微粉末をパウダーフィーダー(MPF)31、32に貯留しておき、マスフローコントローラ(MFC)33、34によって所定の流量でアルゴンキャリアガス35を供給することによってキャリアガス35に原料微粉末が混入した原料(例えば、ZrC1₄ : YC1₃ = 5 : 1の重量比に混合)を配管36を通じて原料蒸気供給管26に対して気密的に回転、スライドできるようにしてある。

【0021】そして外部固定部材(図示せず)に固定されたスライドベース51に係合されたスライド52によって上下垂直方向にスライド自在にモータ53が支持されており、このモータ53の回転出力軸54に回転ねじ体55が垂直軸の周りに水平に回転するように固定されている。回転ねじ体55の下面側には締付けリング56によってLSM基体23の上端部が固定されている。なお、LSM基体23の上部(固体電解質膜を成膜しない部分)には後述する塩化物排気を排出するための通気口23aが複数箇所に形成されているものとする。

【0022】一方、上部にねじ部61が形成され、下部に追うOリング62のはめ込まれたスライドガイド6

3が形成された支持筒体64が反応室21の上端部に固定されている。また支持筒体64には複数の位置に塩化物排気用の通気口65が形成されている。そしてこの支持筒体64のねじ部61に前述の回転ねじ体55が螺合させられている。

【0023】支持筒体64よりも下方の位置において、反応室21の内部に仕切板71が気密的に取り付けられている。この仕切板71の内周部にはOリング72がはめ込まれ、LSM基体23の外周面に気密的に、かつスライド可能に接触させられている。そしてこの仕切板71の上側の位置において反応室21に塩化物排気用の排気口73が形成され、また仕切板71の下側の位置において反応室21に酸化物排気用の排気口74が形成されている。

【0024】なお、原料蒸気供給管26はモータ53、回転出力軸54、回転ねじ体55及び締付けリング56の各中心部を貫通するように配管されており、シーリング手段(図示せず)によって気密的にシーリングされていて、これらモータ53、回転出力軸54、回転ねじ体55及び締付けリング56が原料蒸気供給管26に対して気密的に回転、スライドできるようにしてある。

【0025】次に、上記構成の電気化学蒸着装置による固体電解質成膜の手順について説明する。塩化イットリウムYC1₃、塩化ジルコニアZrC1₄の原料微粉末をパウダーフィーダー(MPF)31、32に貯留しておき、マスフローコントローラ(MFC)33、34によって所定の流量でアルゴンキャリアガス35を供給することによってキャリアガス35に原料微粉末が混入した原料(例えば、ZrC1₄ : YC1₃ = 5 : 1の重量比に混合)を配管36を通じて原料蒸気供給管26に4～10g/hr程度の速度で供給し、ヒータ22の加熱によって原料を気化させ、原料蒸気にして反応室21内のLSM基体23の内側に下部から供給する。

【0026】反応室21内は真空中に近い状態、約1 Torrにして、かつヒータ22によって約1000～1200°Cの温度条件で、空気極支持管となる多孔質のLSM基体23の外側にはアルゴンAr、酸素O₂、水蒸気H₂Oの混合酸化ガス24を0.4～2.0L/minの流量で導入し、内側にはYSZ膜の原料となるイットリウム、ジルコニウムの塩化物YC1₃、ZrC1₄の蒸気25をキャリアガスであるアルゴンArに混入して原料蒸気供給管26の下端部から供給する。これによって、図7に示したCVD-EVD作用によって基体23の内側面に固体電解質膜としてYSZ膜28が成膜される。

【0027】そしてこの原料蒸気25の供給中、モータ53を正逆回転させ、回転出力軸54を介して回転ねじ体55をゆっくりと正逆回転させることによって、反応室21の上部の支持筒体64のねじ部61との螺合により回転ねじ体55を回転させながらモータ53と共に上

下移動させ、これに取り付けられている基体23をも回転させながら上下移動させる。基体23の回転速度は0.005~0.05 rpmの微速である。これによって、原料蒸気25の速度、濃度、反応室21内の温度条件などのばらつきや中心軸のオフセットがあってもYSZ膜28が基体23の内側面の各部に均一な膜厚で蒸着される。

【0028】なお、CVD-EVD法で生まれる塩化物排気41は基体23上部の通気口23a、支持筒体64の通気口65を通じて反応室21内の仕切板71の上側の部屋に集まり、ここから排気口73を通じて外部に排出される。また酸化物排気42は反応室21内の仕切板72の下側に集まり、ここから排気口74を通じて外部に排出される。

【0029】このようにしてこの第1の実施の形態の電気化学蒸着装置を用いた固体電解質成膜方法では、CVD-EVD法に基体23に固体電解質YSZ膜28を成膜する際に、基体23を反応室21内で回転させながら上下に移動させて、反応室21内の上下で、また円周方向で原料蒸気25の速度、濃度、温度条件などのばらつきがあっても、YSZ膜28が基体23の内側面の各部に均一な膜厚で蒸着できる。

【0030】次に、本発明の第2の実施の形態の電気化学蒸着装置を図3に基づいて説明する。第2の実施の形態の電気化学蒸着装置は、原料液貯留部81, 82を備え、原料微粉末である塩化イットリウムYC13と塩化ジルコニウムZrC14、それぞれを希釈剤としてのエタノールによって希釈して混合液にしてここに一時的に貯留する。この原料液貯留部81, 82に貯留される原料液はマスフローコントローラ(MFC)83, 84それぞれによって一定時間に一定量を排出するように制御する。

【0031】反応室21の構造と反応室21内の基体23に対する回転、スライド機構の構造は図1、図2に示した第1の実施の形態と同じである。

【0032】次に、この第2の実施の形態の電気化学蒸着装置を用いた固体電解質成膜の手順について説明する。塩化イットリウムと塩化ジルコニウムとの微粉末それぞれを適当な量のエタノールと混合して原料混合液を作成し、これらを原料液貯留部81, 82それぞれに貯留させる。

【0033】反応室21は真空に近い気圧、約1 Torr程度まで減圧し、さらにヒータ22によって1000~1200°Cの温度まで加熱する。そしてアルゴン、水蒸気及び酸素の混合酸化ガス24を0.4~2.0 l/minの流量で反応室21内の基体23の外側に供給する。

【0034】こうした予備工程の後、原料貯留部81, 82に貯留されている原料液に対して、マスフローコントローラ83, 84によってアルゴンガスを所定流量で

供給してこれらの原料液を、例えば、両方の原料液の供給量がその中に含まれる原料粉末の重量に換算して合計で4~10 g/hr程度の流量で供給し、図示していない気化室で加熱して希釈剤を蒸発分解させ、さらに残った塩化イットリウム、塩化ジルコニウムを気化させた後、キャリアガスであるアルゴンガスArと共に原料蒸気供給管26に供給し、この原料蒸気供給管26から原料蒸気25を反応室21内のLSM基体23の内側に下部から供給する。

10 【0035】そしてこの原料蒸気25の供給中、モータ53を回転させ、回転出力軸54を介して回転ねじ体55をゆっくりと回転させることによって、回転ねじ体55と共に基体23を回転させながら上下移動させる。

【0036】この手順を所定時間、例えば5時間繰り返すことにより、第1の実施の形態と同様にCVD-EVD作用によって基体23の内側面に固体電解質膜としてYSZ膜28を成膜することができる。しかも、原料蒸気25の速度、濃度、反応室21内の温度条件などのばらつきがあっても、基体23が回転しながら上下移動するのでYSZ膜28が基体23の内側面の各部に均一な膜厚で蒸着させることができる。

【0037】

【実施例】<実施例1>図1及び図2に示した電気化学蒸着装置を用いてYSZ固体電解質の成膜を行った。そのため、空気極支持管をなす基体23のLSM管(外径21mmφ、内径17mmφ、長さ50cm)を反応室21において回転ねじ体55の下部に取り付け、また外径12mmφ、内径9mmφのカーボン製の原料蒸気供給管26を反応室21の中心部に取り付けた。そして、反応室21を1 Torr程度まで真空にし、ヒータ22によって1200°Cに加熱し、さらに反応室21の基体23の外側にアルゴン/水蒸気/酸素の酸化ガス24を0.5 l/minの流量で供給した。

【0038】そしてマスフローコントローラ33, 34によって塩化イットリウム、塩化ジルコニウムそれぞれの微粉末を1:5の重量比で、かつ原料粉末重量に換算して両方で5 g/hr程度となる流量で気化室(図示せず)に供給して1200°Cに加熱して気化させて原料蒸気とし、これをさらに原料蒸気供給管26から反応室2

40 1の基体23の内側に供給し、5時間の電気化学蒸着を行い、約50 μmのYSZ固体電解質膜28を成膜した。この電気化学蒸着の間、モータ53によって原料蒸気供給管26を0.01 rpmでゆっくりと正逆回転させることによって最下位置から最上位置まで上下移動させた。

【0039】得られた固体電解質膜は緻密で均一な膜厚であった。

【0040】<実施例2>図3に示した電気化学蒸着装置を用い、塩化イットリウム、塩化ジルコニウムそれぞれの微粉末をエタノールと重量比で1:1に混合した原

料液を1:5の割合で、かつ原料粉末重量に換算して両方で5g/h程度となる流量で装置に供給し、120°Cに加熱して希釗剤を蒸発分解し、また原料粉末を気化させて原料蒸気にし、これを実施例1と同じく1Torr程度の真空で、1200°Cに加熱した反応室21の基体23の内側に原料蒸気供給管26を通じて供給しつつ、電気化学蒸着を行った。基体23の回転速度の設定は実施例1と同じにした。

【0041】得られたYSZ固体電解質膜28は約50μmであり、緻密で均一な膜厚であった。

【0042】

【発明の効果】以上のように請求項1の発明の電気化学蒸着装置によれば、蒸着原料粉末を気化させて反応室に導入して蒸着基体の内周面に電気化学蒸着させる際に、蒸着基体を軸周りに回転させ、かつ軸方向に移動させることによって、反応室内の蒸着原料蒸気の流れや酸化ガスの流れが不均一であっても蒸着基体の表面各所に均一な膜厚で蒸着原料蒸気を蒸着させ、膜厚の均一な固体電解質を成膜することができる。

【0043】請求項2の発明の固体電解質の成膜方法によれば、請求項1の発明の電気化学蒸着装置を用いて蒸着基体の内周面に固体電解質膜を成膜するので、蒸着基体の内周面全体に渡り、均一な膜厚の固体電解質膜を成膜することができる。

【図面の簡単な説明】

【図1】本発明の第1の実施の形態の電気化学蒸着装置の断面図。

【図2】上記の実施の形態の電気化学蒸着装置の基体回転・移動機構部分の拡大断面図。

【図3】本発明の第2の実施の形態の電気化学蒸着装置の断面図。

10 21 反応室

22 ヒータ

23 基体

24 酸化ガス

25 原料蒸気

26 原料蒸気供給管

28 YSZ膜

31 パウダーフィーダ

32 パウダーフィーダ

33 マスフローコントローラ

34 マスフローコントローラ

51 スライドベース

52 スライダ

53 モータ

54 回転出力軸

55 回転ねじ体

61 雄ねじ部

63 スライドガイド

64 支持筒体

73 排気口

74 排気口

81 原料液貯留部

82 原料液貯留部

30 83 マスフローコントローラ

84 マスフローコントローラ

【図4】従来の円筒固体電解質型燃料電池の斜視図。

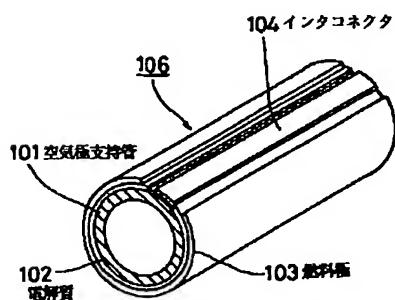
【図5】他の従来の円筒固体電解質型燃料電池の断面図。

【図6】従来の電気化学蒸着装置の断面図。

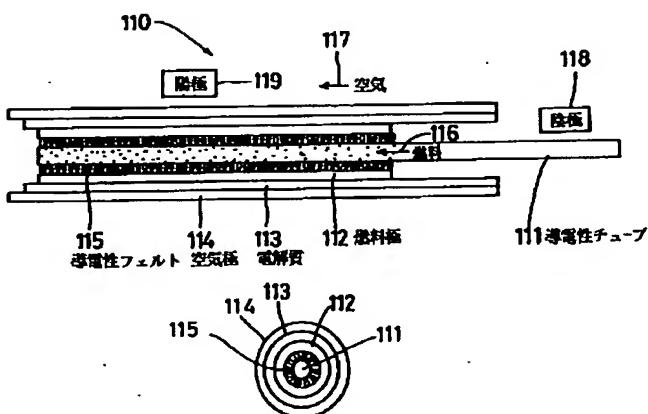
【図7】一般的な電気化学蒸着作用の説明図。

【符号の説明】

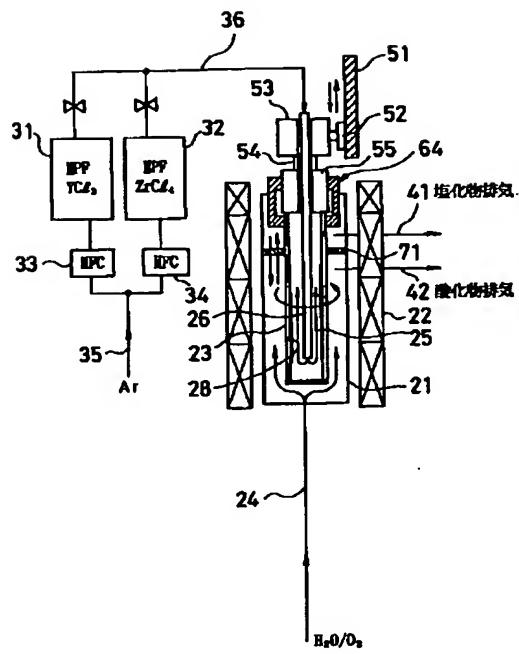
【図4】



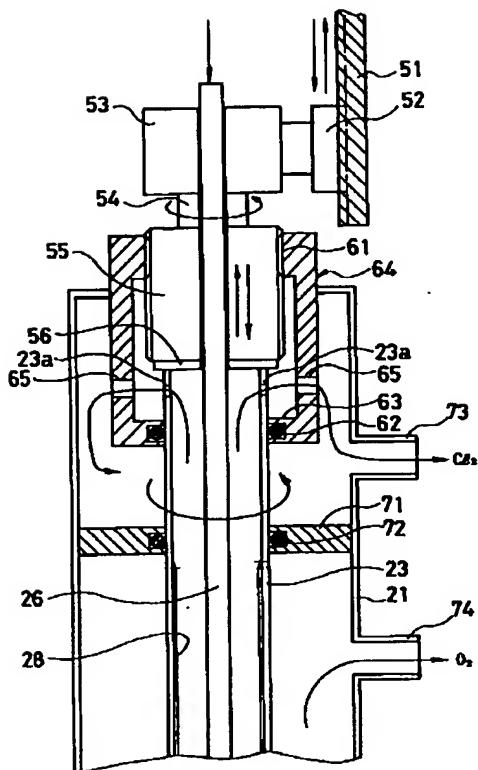
【図5】



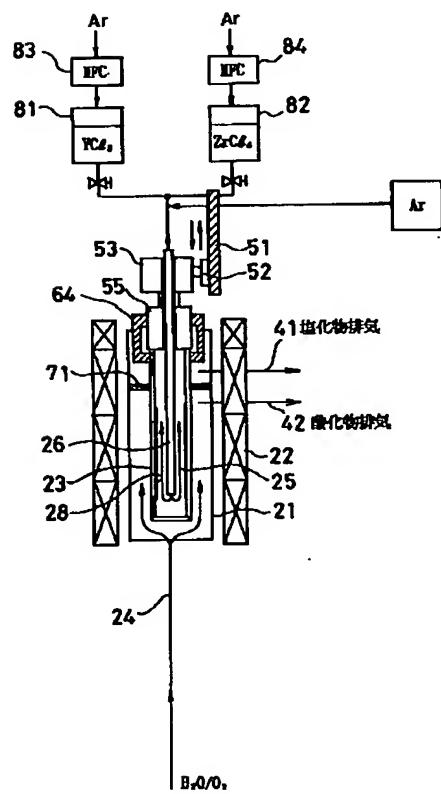
【図1】



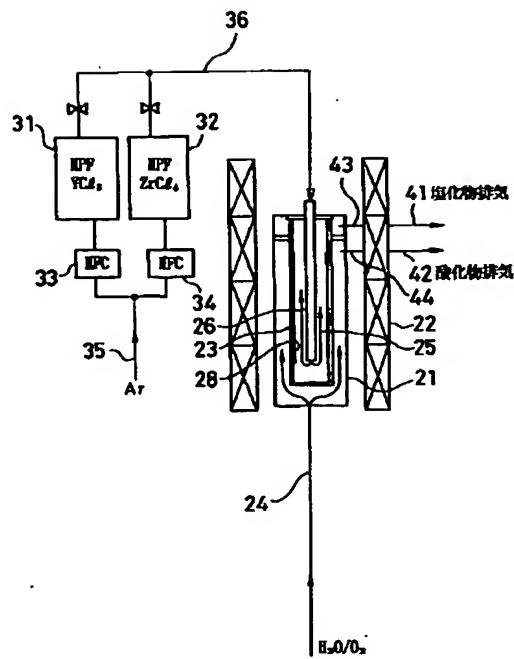
【図2】



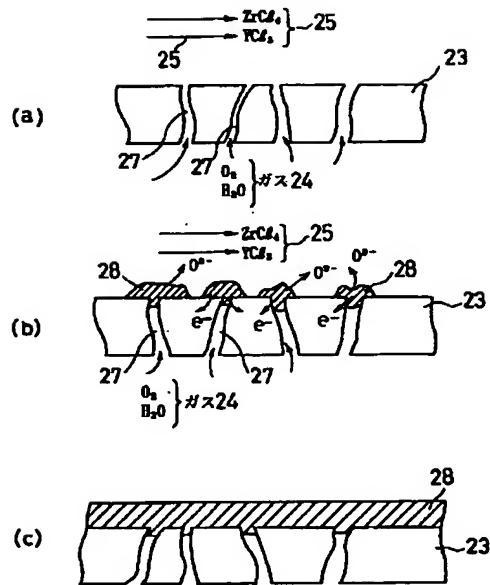
【図3】



【図6】



【図7】



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